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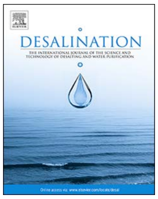

Studies on the properties of RO membranes for salt and boron removal: Influence of thermal treatment methods and rinsing treatments

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ABSTRACT

The physicochemical properties and performance of thin film composite (TFC) membranes depend on its synthesis conditions. In this study, TFC membranes were fabricated using interfacial polymerization (IP) method and the effects of heat treatment methods and post-IP rinsing (prior to heat curing step) on the membrane performances were investigated. Keeping the substrate in minimal heat exposure could prevent substrate pore annealing that potentially reduces the membrane water permeability. Evidently, the membranes with only polyamide (PA) layer being heat-treated exhibited > 250% enhancement in pure water flux (PWF) compared to the membranes where both PA and substrate layer were heat-treated. Also, the membranes rinsed with pure n-hexane tended to display higher PWF without significantly decreasing solute rejection, possibly due to the reduced membrane cross-linking following the removal of unreacted monomers and excess solvent from the membrane surface. The membrane performance became practically the same after post-IP rinsing, regardless of the solvent used in the IP reaction, suggesting that the disparity in the membrane performance is mainly caused by the difference in solvent evaporation rate during heat treatment. The variations in solvent surface tension and viscosity during the IP reaction meanwhile did not play a key role affecting PA layer chemistry and performance.

1. Introduction

Over the years, reverse osmosis (RO) has been widely adopted as an advanced separation process in desalting saline water owing to the tremendous progress in membrane technology. Saline water desalination was firstly made practicable with the introduction of the first RO membrane, known as the cellulose acetate (CA) membrane by Loeb and Sourirajan in the 1960s. Back then, it was reported that CA membrane could reject ~99% of salt from salty feed solution [1]. Nevertheless, the usage of CA membrane was restricted as it suffered from low water permeability (~0.14 $L/m^2 \cdot h \cdot bar$) and low chemical and pH tolerance. In addition, the asymmetric membrane required high operating pressure (> 135 bar) to produce salt-free water.

A decade later, the fate of RO changed when Cadotte and his colleagues introduced a novel membrane called the thin film composite (TFC) membrane. At an operating pressure of ~69 bar, the membrane showed high water permeability (~0.74 $L/m^2 \cdot h \cdot bar$) at similar salt rejection as the CA membrane [2]. In addition, the TFC membrane also showed better chemical and pH tolerance, etc. Following the usage of TFC membranes, saline water desalination became a viable option in producing freshwater. To date, the TFC membrane remains as the dominant choice for saline water desalination worldwide.

Typical TFC membranes consist of three layers, that include i) an ultrathin semipermeable polyamide (PA) selective layer, synthesized using interfacial polymerization (IP) on top of ii) a microporous substrate that is reinforced by iii) a non-woven polyester fabric [3]. In the TFC membranes, it is the top PA layer that governs the membrane water permeability and salt rejection while the microporous substrate and the non-woven fabric act as the supporting layers. In this regard, slight changes to the chemical structure and morphology of the PA layer could alter the performance of the resultant membrane [4]. Since the physicochemical properties of TFC membranes are closely related to the synthesis conditions, extensive research was conducted in the past to investigate the effect of IP conditions on the properties and performance of the resultant membranes. These include varying the type of monomers [5–7], incorporating organic or inorganic additives into membrane [8–13] and changing reaction time between two monomers [14–16]. The review on the development of TFC membranes can also be

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found elsewhere [17–18].

In addition, comprehensive studies have also been directed to investigate the relationship between heat treatment conditions and the performance of TFC membranes [3,4,19]. In these studies, it was demonstrated that heat treatment following IP reaction is necessary to complete the formation of PA layer. It helps increasing membrane water flux and salt rejection by removing residual organic solvent from the PA film and promoting additional cross-linking through dehydration of amine and carboxylic acid residues [19]. Nonetheless, membrane heat treatment should be controlled as overheating the membrane (i.e., heating the membrane significantly longer than the minimum time or at too high temperature) may result in shrinkage or annealing of support membrane pores, leading to decreased membrane water permeability.

According to Ghosh et al. [19], the optimal heat treatment time and temperature depend on the volatility of the organic solvent used in synthesizing the PA layer. In view of this, post-IP treatment (step before heat treatment) such as rinsing membrane surfaces with solvent(s) could potentially alter the properties of the resultant membrane. However, a comprehensive investigation on the effect of post-IP treatment on the PA chemistry and membrane performance (made at various water-organic solvent system) is currently not available. Moreover, although heat treatment following IP reaction was widely adopted in the fabrication of TFC membranes, the effect of membrane heat treatment methods on the membrane performance, as well as the uniformity of the membrane formed has not been discussed in the past.

In the present study, the effects of heat treatment methods (membrane is heated either only at the top side or both top and bottom sides) and post-IP rinsing on the physicochemical properties and RO performance of TFC membranes were fully investigated. For this purpose, the effect of heat treatment methods was investigated first whereby TFC membranes were synthesized under the same IP conditions, but heat-treated using different fabrication setups. The method that provides the most satisfactory results would be adopted in the study of post-IP rinsing, in which different solvents were used for the preparation of the organic phase in the IP reaction, followed by post-IP rinsing with hexane in one series of membrane fabrication, while no post-IP rinsing was applied in another series for comparison. All membranes fabricated were evaluated with respect to pure water flux (PWF), salt and boron rejection. The filtration results were verified by a systematic membrane characterization using FESEM and contact angle analyzer.

2. Materials and methods

2.1. Chemicals and reagents

Polysulfone (PSf) microporous substrate reinforced with a polyester non-woven fabric (molecular weight cut-off of 20 kDa) was purchased from RisingSun Membrane Technology (Beijing) Co. Ltd. and used as the supporting layer for the formation of PA selective layer. Meta-phenylenediamine (MPD) and trimesoyl chloride (TMC) from Merck and Acros Organics, respectively were used as the monomers for the formation of PA layer. n-hexane and n-heptane from Merck, cyclohexane (Fisher Scientific) and Isoparaffin-G (Isopar, Exonmobil) were used as solvents to dissolve TMC monomer. Sodium chloride (NaCl, Merck), calcium chloride ($CaCl_2$, Fluka) and boric acid (Fisher Scientific) were used as test solutes for membrane flux and rejection determination. Sulfuric acid (98%, Merck) and BoroVer 3 boron reagent powder (Hach) were used to determine boron concentration in aqueous solutions. Milli-Q® RO water was used to prepare all the feed solutions for membrane performance evaluation. All chemicals acquired are of analytical grade and were used as received without further purification.

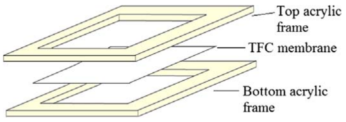
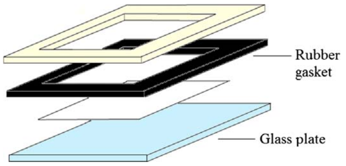
2.2. Preparation of thin film composite membrane

TFC membranes were fabricated via IP process. Prior to the IP process, commercial PSf microporous substrate was soaked in RO water for 24 h to remove glycerin. The wetted substrate (dimension: 13.5 cm × 13.5 cm) was placed on a glass plate followed by removing the excess water from its top surface using a soft rubber roller. Next, a rubber gasket together with an acrylic frame was placed on top of the substrate. The glass plate-membrane-gasket-frame stack (hereafter known as the frame setup) was held together using binder clips.

To initiate IP process, 30 mL of 2 w/v% aqueous MPD solution was poured into the frame and allowed to contact with the PSf substrate for 2 min before draining it off. The rubber gasket and acrylic frame were then disassembled and the aqueous MPD solution residing on the top layer of the substrate was removed gently using a rubber roller. It is imperative to ensure that no water droplets remain on the substrate surface as any water droplets residing on top of the substrate surface may lead to the formation of micro or macro-voids in the selective layer. Soon after the substrate surface was rolled dry, the rubber gasket and acrylic frame were reassembled. 30 mL of 0.1 w/v% of TMC in n-hexane was poured onto the substrate top layer to allow it to react with the amine monomer. Excess TMC solution was poured away after 1 min of reaction time. It was followed by rinsing the membrane surface with 30 mL of pure n-hexane to remove any unreacted MPD and TMC monomers. Subsequently, the membrane was removed from the frame setup, placed in between two acrylic frames and heat-treated in an oven at 60 °C for 10 min. This fabrication setup is named as Method A (Table 1) hereafter. At last, the heat-cured membrane was stored in RO water until further use.

To study the effect of heat treatment methods on the membrane performance, two additional heat treatment methods, i.e., i) keeping membrane in the frame setup – heat treat the membrane immediately after 1 min of IP reaction (Method B) and ii) adding a piece of wet tissue in between the glass plate and membrane was adopted in fabricating TFC membranes (Method C). Illustrations of both fabrication setups are provided in Table 1. Heat-treating the membrane in the single frame (Method B) or two-frame setup (Method A) is commonly applied by researchers in fabricating TFC membranes. Meanwhile, the method of placing wet tissue (or other water absorbing material) underneath the membrane prior to heat curing has rarely been reported. This protocol was previously reported by Loeb and Sourirajan in an attempt to improve the desalinization performance of a commercial CA membrane by means of differential heating [1]. They inserted a piece of wet filter paper underneath the CA membrane prior to the contact with boiling water or steam and was found that the wet filter paper helped in keeping the smooth side of the CA membrane cool, without shrinking

Table 1
TFC membrane heat treatment methods.

Method	Description	Illustration of fabrication setup
A	Placing membrane in between two acrylic frames. Both sides of membrane are directly exposed to heating.	
B	Keeping membrane in the frame setup. Only the top surface of membrane is directly exposed to heating.	
C	Adding a piece of wet tissue underneath the membrane in Method B. This is to further reduce the heating rate on the bottom surface of membrane.